Electrochemical detection of bisphenol A mediated by $[Ru(bpy)_3]^{2+}$ on an ITO electrode

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ABSTRACT

A simple strategy for the direct and indirect detections of bisphenol A (BPA) at an ITO electrode is described. The direct determination of BPA in buffer solution of pH 7.2 is accomplished by the application of differential pulse voltammograms with the anodic peak at 0.546 V. The indirect approach is based on the mediation of $[Ru(bpy)_3]^{2+}$ (where bpy = 2,2′-bipyridine), which is served as an excellent catalyst to induce the oxidation of BPA. By monitoring the peak current of $[Ru(bpy)_3]^{2+}$–BPA complex, the mediated detection of BPA is successfully carried out. The response current exhibits a linear range between 5 and 120 μmol L^{-1} with a high sensitivity (0.22 μA μmol^{-1} L). The detection limit of BPA is 0.29 μmol L^{-1} (S/N = 3), which is larger than that analyzed by gas chromatography–mass spectrometry, however this detection method not only has the advantages of low cost and simple operation, but also provides a powerful basis for removing BPA. In addition, according to the effects of pH, scan rate and mediator concentrations on the voltammetric responses of BPA oxidation, the oxidized mechanism of BPA in the presence of $[Ru(bpy)_3]^{2+}$ on the ITO electrode is discussed in detail.

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1. Introduction

There is an increasing concern about endocrine-disrupting chemicals released into the environment. Bisphenol A (BPA), 2,2-*bis*(4-hydroxyphenyl) propane, has estrogenic activity and is acutely toxic to aquatic organisms [1,2]. It is commonly used as a raw material in the manufacture of polycarbonate and epoxy resins, or as an antioxidant and stabilizing agent for numerous plastic [3–5]. In recent years, BPA and its derivatives have been widely distributed in the natural environment and surface water. Thereby, it is quite urgent to search an efficient approach for the degradation and detection of such a chemical so as to minimize its contamination [6–8].

Various treatment techniques for wastewater, which contains BPA and other phenolic compounds have been developed, using chemical, biological, photochemical and electrochemical procedures [9–12]. Compared with the chemical or biological methods, the electrochemical technique for removing organic pollutants has few or no harmful effects on the environment, it is more independent conditions of wastewater [13,14]. Recently, many attempts have been made to study the electrochemical removal of BPA using various electrodes such as Pt/Ti [15,16], SnO$_2$/Ti [17], Au [18], car-

bon fiber [19,20], and boron-doped diamond [21]. Fenton's reagent generated by an electrochemical technique has been used for the degradation of BPA [22]. However, the electrochemical oxidation of BPA and other phenolic compounds may cause the inactivation of carbon or noble metal electrodes due to the deposition of electropolymerized films [23,24]. In order to efficiently treat the phenolic effluents, it is necessary to avoid the passivation of electrodes and remove the strongly adherent polymer film.

On the other hand, electrochemical polymerization of phenolic compounds has been used in electrochemical sensors [25–27]. Compared with chemical sensors, chromatographic methods, and biological assays [28–33], the electrochemical method has the advantages of low cost and simple operation. Several kinds of electrodes such as Pt, glassy carbon, TiO$_2$ and polypyrrole have been used for the oxidation and determination of BPA [34–38]. Based on the rich redox activities and well-known luminescence properties of polypyridyl ruthenium(II) complexes [39,40], they have been electrochemically used as novel probes of DNA [41–43], guanine [43–45] and hypoxanthine [46,47]. However, to our knowledge, there is no report on the electrochemical oxidation and detection of BPA mediated by the ruthenium(II) complexes.

Herein, we extend voltammetric techniques to study the detection of BPA and explore the direct and mediated oxidation of BPA by $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine). In order to reduce the effect of solvent water molecules on the detection of BPA, an indium-tin oxide (ITO) is preferred as working electrode. Fortunately, by controlling the potential range of differential pulse voltammetric

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sweeping in the presence of $[Ru(bpy)_3]^{2+}$, the direct and mediated detection of BPA with a high selectivity is achieved. The oxidized mechanism of BPA mediated by $[Ru(bpy)_3]^{2+}$ is also studied in detail. This study provides a powerful basis for the detection and degradation of BPA.

2. Materials and methods

2.1. Chemicals and materials

All chemicals were of reagent grade and purchased from commercial vendors. $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ and bisphenol A (BPA) from Sigma Co. were used as received. The electrolyte solutions were $0.2 \, mol \, L^{-1}$ HCl or buffer system of pH 7.2 containing $10 \, mmol \, L^{-1}$ Tris (tris-hydroxy methyl amino-methane) and $50 \, mmol \, L^{-1}$ NaCl by preparing with double-distilled water. And BPA stock solutions of $0.2 \, mmol \, L^{-1}$ were stored at room temperature.

2.2. Method and experimental conditions

Voltammetric measurements were performed on a CHI660a electrochemical system with a corresponding software package (Shanghai, China). Emission spectra were performed on a Hitachi RF-2500 fluorescence spectrophotometer. The excitation wavelength of 450 nm was used. The fluorescence images were taken using a Nikon Eclipse TS100 inverted fluorescence microscope system (Japan), equipped with a 50 W mercury lamp source. The images were captured with a Nikon E4500 camera at an excitation of blue light. The SEM images were recorded on a LEO 1450 VP scanning electron microscope.

The electrochemical experiment was performed using cyclic voltammetry or differential pulse voltammetry in a single-compartment cell of 0.20 mL. The working electrode is an indium-tin oxide (ITO)-coated glass plate (sheet resistance $\approx 20 \, \Omega \, cm^{-2}$) from Shenzhen Nanbo Co. Ltd., China. The ITO surface of $0.40 \, cm^2$ was exposed to electrolyte solutions and its electron conduction was made by gluing a piece of thin copper belt and sealed externally with the polytetrafluoroethylene belt. Effective area of the ITO electrode was $0.41 \, cm^2$, determined by cyclic voltammograms of $0.1 \, mmol \, L^{-1}$ $K_4[Fe(CN)_6]$ in $1.0 \, mol \, L^{-1}$ KCl with the diffusion coefficient of $6.3 \times 10^{-6} \, cm^2 \, s^{-1}$ [48]. Prior to using the ITO electrode, it was cleaned by ultrasonic in double-distilled water for 15 min. A platinum wire was used as an auxiliary electrode and the potential was measured with reference to an Ag-AgCl electrode with $50 \, mmol \, L^{-1}$ NaCl.

All the experiments were performed at room temperatures (22–24 °C).

3. Results and discussion

3.1. Direct detection of BPA on the ITO electrode

The first differential pulse voltammograms (DPVs) for the oxidation of bisphenol A (BPA) in buffer solution of pH 7.2 on the ITO electrode are shown in Fig. 1a. A well-defined wave (peak I) is observed at a peak potential of 0.546 V, ascribed to the irreversible oxidation of neutral BPA based on the acid dissociation constant of 9.8 [49]. With decreasing pH, the oxidative wave of BPA is shifted to a more positive potential due to the weakened deprotonation as shown in Fig. 1b. In acidic medium containing $0.2 \, mol \, L^{-1}$ HCl, BPA is oxidized at a peak potential of ca. 1.028 V. The value shows a positive shift of 0.482 V compared with that in neutral medium. Interestingly, with increasing BPA concentrations up to $0.12 \, mmol \, L^{-1}$, the response current linearly increases with the correlation coefficient of 0.994 and the regression line passes
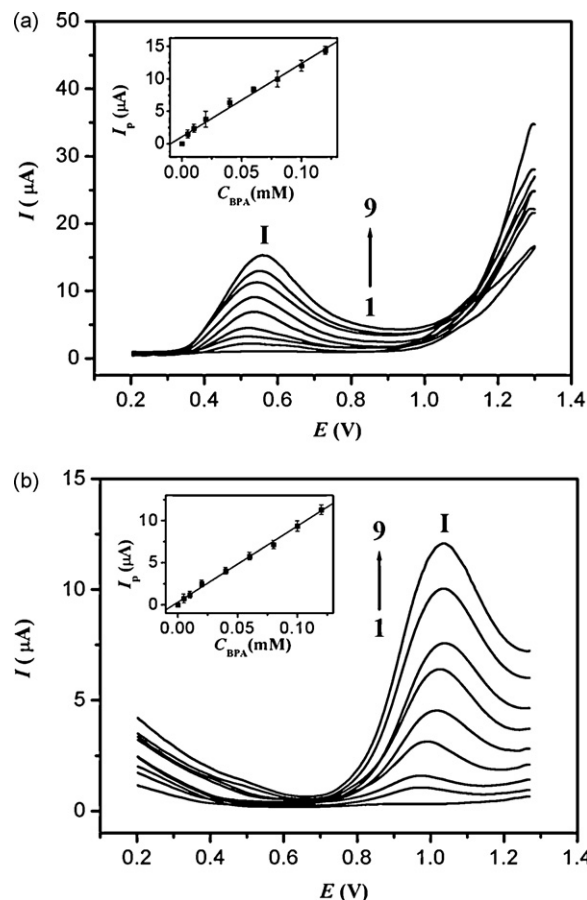

Fig. 1. The first DPVs of BPA on the ITO electrode in buffer solution of pH 7.2 (a) and $0.2 \, mol \, L^{-1}$ HCl (b). BPA concentrations (mmol L^{-1}): (1) 0, (2) 0.005, (3) 0.01, (4) 0.02, (5) 0.04, (6) 0.06, (7) 0.08, (8) 0.10, (9) 0.12. The inset is a plot of the peak I currents vs BPA concentration.

the origin. The results provide a powerful basis to carry out the direct detection of BPA on the ITO electrode.

It has been reported that the electrochemical oxidation of BPA and other phenolic compounds causes the inactivation of graphite [23], glassy carbon [37], carbon fiber [50], and noble metal electrodes [24]. It is interesting to know whether BPA or its oxidized product could be adsorbed on the ITO electrode surface and further influence the ITO activity. Fig. 2a gives the progressive DPVs of BPA in buffer solution of pH 7.2, the peak current indicates an obvious decrease and completely disappears in subsequent cycles. Furthermore, the SEM images in Fig. 3a show that the oxidized product of BPA obtained by repetitive DPVs is a compact appearance and hence the oxidation of BPA is blocked. On the other hand, as depicted by Fig. 4, while the ITO electrode is pretreated for different time at an applied potential of 0.6 V or 0.2 V, the first DPVs show a decreased current at 0.6 V with increasing time and no effect is observed at 0.2 V. The result reveals that the oxidized products of BPA may be strongly adsorbed on the ITO surface, leading to a decrease in the activity of ITO electrode. The positive shift of peak I with increasing BPA concentration depicted by Fig. 1 further confirms these observations.

According to the analysis mentioned above, if assuming the charge from the first scan to be one electron transfer in the process of BPA oxidation, the direct oxidation of BPA on the ITO electrode is proposed as follows (where BPA_{Ox} represents the oxidized product of BPA):

$$BPA - e \underset{ITO}{\rightleftharpoons} BPA_{Ox}/ITO \tag{1}$$
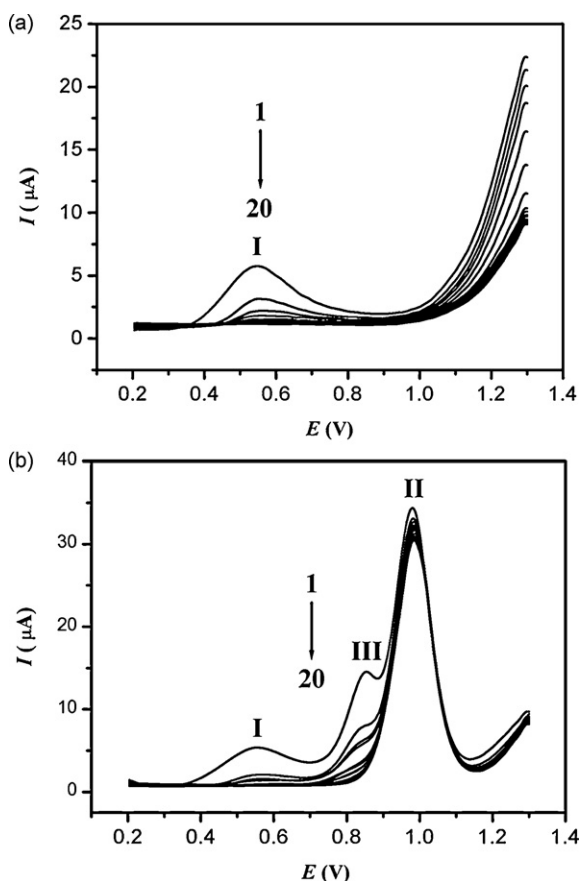
Fig. 2. Progressive DPVs of 0.06 mmol L^{-1} BPA (pH 7.2) on the ITO electrode in the absence (a) and presence (b) of 0.2 mmol L^{-1} [Ru(bpy)$_3$]$^{2+}$.

3.2. Mediated detection of BPA by [Ru(bpy)$_3$]$^{2+}$

As depicted by curve 1 of Fig. 5a, the DPV of [Ru(bpy)$_3$]$^{2+}$ on the ITO electrode in neutral medium shows a well-defined anodic wave (peak II) at 0.990 V, ascribed to the oxidation of [Ru(bpy)$_3$]$^{2+}$. The reactive process is written as follows:

$$[Ru(bpy)_3]^{2+} - e \underset{ITO}{\rightleftharpoons} [Ru(bpy)_3]^{3+} \qquad (2)$$
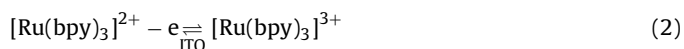
When BPA is added to the test system, two other anodic waves (peak I and peak III) are observed (curves 2–8), respectively. Compared with the oxidation of BPA alone (dotted line), the peak I at 0.554 V (0.06 mmol L^{-1} BPA) is considered as the direct oxidation of BPA on the ITO surface. While BPA concentrations are changed in the range from 5 to 120 μmol L^{-1}, the response current of BPA (peak I) on the ITO electrode exhibits an enhancement. The result is similar to that in the absence of [Ru(bpy)$_3$]$^{2+}$, implying that the presence of [Ru(bpy)$_3$]$^{2+}$ hardly affects the direct oxidation of BPA on the ITO electrode. More interestingly, as depicted by Fig. 5a, the height of peak III also increases with the rise of BPA concentration, showing a linear relation with the correlation coefficient of 0.995. The response sensitivity is 0.22 μA μmol^{-1} L, taken as the average slope of three parallel experiments with the relative standard deviation (RSD%) of 1.14% ($n = 3$). This linear range experiment provides the necessary information for estimating the limits of detection, based on the lowest detectable peak that has a signal-to-noise ratio of three (S/N = 3) cited from IUPAC recommendations [51]. The detection limit of BPA mediated by [Ru(bpy)$_3$]$^{2+}$ is 0.29 μmol L^{-1}. Although this value is larger than that analyzed by gas chromatography–mass spectrometry [50], the
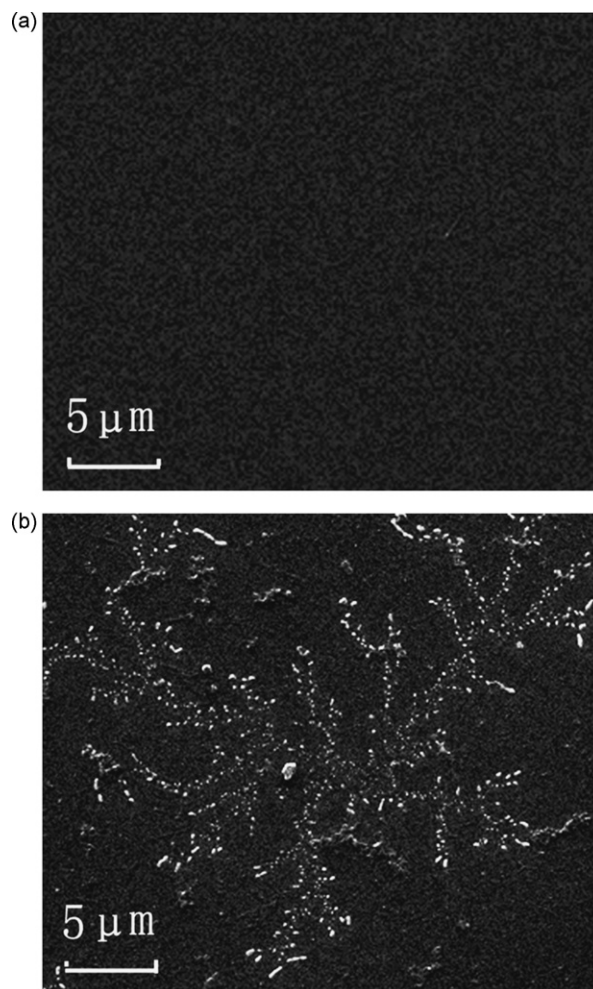

Fig. 3. SEM images of BPAox/ITO (a) and [Ru(bpy)$_3$]$^{2+}$–BPAox/ITO (b), obtained by progressively DPVs of 20 cycles in buffer solution containing 0.06 mmol L^{-1} BPA and 0.1 mmol L^{-1} [Ru(bpy)$_3$]$^{2+}$/0.06 mmol L^{-1} BPA, respectively.

detection method not only has the advantages of low cost and simple operation, but also provides a powerful basis for removing BPA.

On the other hand, in order to explain the peak III reaction, Fig. 6 shows the fluorescence spectra and fluorescence microscopic images of [Ru(bpy)$_3$]$^{2+}$ immobilized on the ITO surfaces in the absence and presence of BPA. The presence of BPA not only weakens the photoluminescence intensity of [Ru(bpy)$_3$]$^{2+}$, but also alters its long-bar morphology. This finding distinctly demonstrates that [Ru(bpy)$_3$]$^{2+}$–BPA complex is formed and hence the peak III may be attributed to the anodic wave of BPA mediated by [Ru(bpy)$_3$]$^{2+}$.

When 0.2 mol L^{-1} HCl is instead of the buffer solution with pH 7.2, the peak potential is positively shifted to 1.028 V for BPA oxidation (peak I) due to its protonation (dotted line in Fig. 5b). In the presence of [Ru(bpy)$_3$]$^{2+}$, only two anodic waves (peaks II and III) are observed, attributed to the oxidation of [Ru(bpy)$_3$]$^{2+}$ and BPA mediated by [Ru(bpy)$_3$]$^{2+}$ in acidic medium, respectively. It is noteworthy that the peak III current also exhibits a linear range between 5.0 and 120 μmol L^{-1} with a sensitivity of 0.35 μA μmol^{-1} L as shown in Fig. 5b. The detection limit is 0.16 μmol L^{-1} (S/N = 3). On the other hand, the baseline of peak II increases with increasing peaks I and III, but the reactive current of peak II becomes lower. As depicted in the inset in Fig. 5, with the rise of BPA concentration from 5.0 to 120 μmol L^{-1}, the peak II current shows a linear decrease, revealing that a new kind of complex "[Ru(bpy)$_3$]$^{2+}$–BPA" is formed by interactions [Ru(bpy)$_3$]$^{2+}$ with BPA, as a result, leading to a decrease of peak II and an increase of peak III. Obviously, this
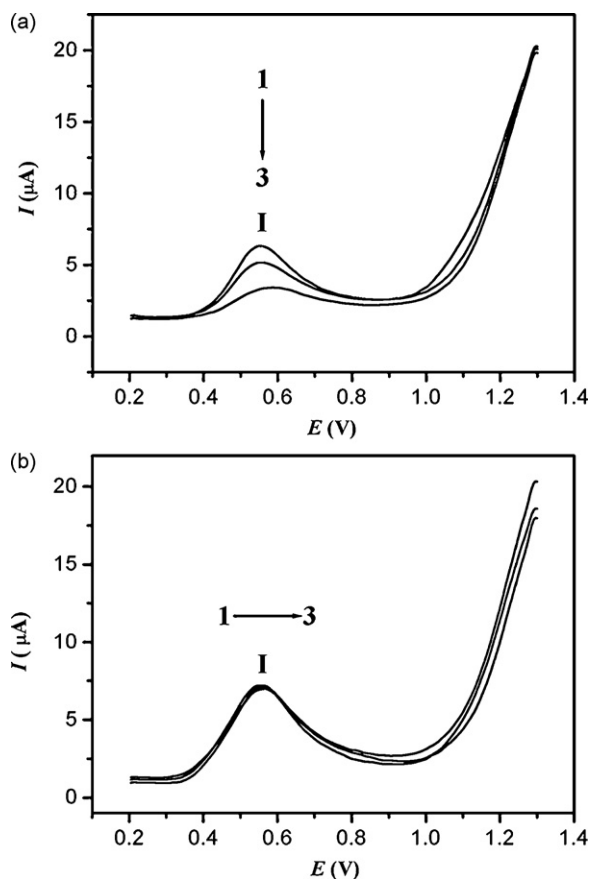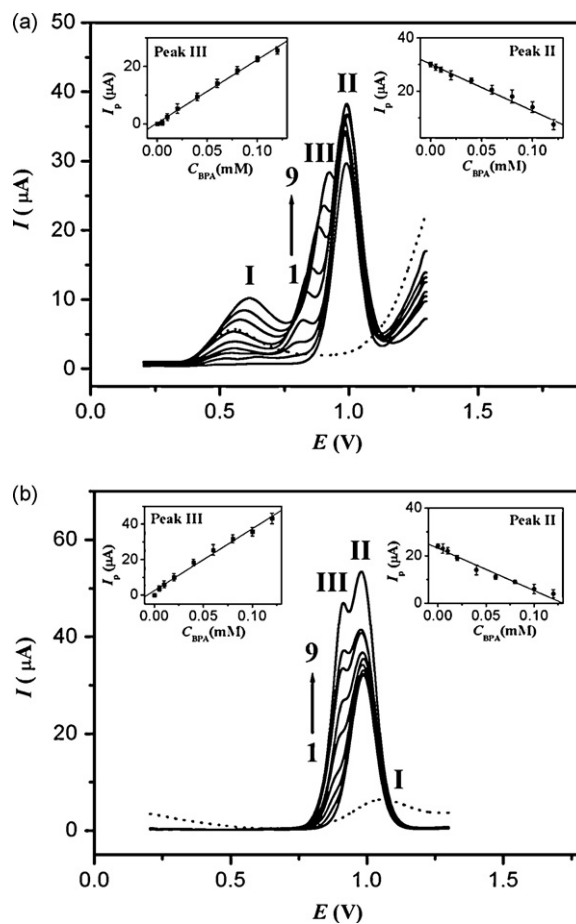
Fig. 4. The first DPVs of 0.06 mmol L^{-1} BPA in buffer solution of pH 7.2 on the ITO electrode at applied potentials of 0.6 V (a) or 0.2 V (b) for different time (s): (1) 0, (2) 20, (3) 100.

Fig. 5. The first DPVs of 0.2 mmol L^{-1} [Ru(bpy)$_3$]$^{2+}$ on the ITO electrode in buffer solution of pH 7.2 (a) and 0.2 mol L^{-1} HCl (b) in the presence of BPA (mmol L^{-1}): (1) 0, (2) 0.005, (3) 0.01, (4) 0.02, (5) 0.04, (6) 0.06, (7) 0.08, (8) 0.10, (9) 0.12. The dotted line corresponds to DPV of 0.06 mmol L^{-1} BPA. The inset shows the current values of peaks II and III as a function of BPA concentration.

finding provides a new way to carry out the indirect detection of BPA.

In order to explore the oxidized mechanism of BPA by [Ru(bpy)$_3$]$^{2+}$, Fig. 7 gives their DPVs on the ITO electrode in 0.2 mol L^{-1} HCl. The dotted line shows the directly oxidized peak I of BPA. With increasing [Ru(bpy)$_3$]$^{2+}$ concentration, peak I subsequently disappears and instead peak III gradually appears on the DPVs. To further illustrate the peak III reaction, Fig. 8 shows the CVs of 0.2 mmol L^{-1} [Ru(bpy)$_3$]$^{2+}$ with increasing BPA concentration in 0.2 mol L^{-1} HCl. At 0.05 V s^{-1} scan rate, a clear peak III emerges on the CVs as well as a pair of redox waves (peak II). The peak current shows a linear increase with BPA concentration, implying that the cyclic voltammetry also can be employed to detect BPA mediated by [Ru(bpy)$_3$]$^{2+}$. Moreover, it is found that the electrochemical behavior of the two peaks is different. It has been known that peak II reaction conforms to the characteristic of diffusion-controlled wave. However, peak III reaction only presents an anodic process, no cathodic wave is observed. At 0.80 V s^{-1} high scan rate, although the peak current shows a linear enhancement with increasing BPA concentration, the peak III potential exhibits a positive shift and hence the peaks II and III indicate a part overlap. These results reveal that the peak III reaction may be considered as an irreversible reaction of [Ru(bpy)$_3$]$^{2+}$–BPA complex. Also, as depicted by Fig. 9, when BPA concentration is fixed at 0.06 mmol L^{-1}, the peak III current shows a gradual enhancement with increasing [Ru(bpy)$_3$]$^{2+}$ concentrations at both 0.05 and 0.80 V s^{-1}. The result further illustrates that the reaction of peaks II and III is interdependent and peak III corresponds to the anodic reaction of [Ru(bpy)$_3$]$^{2+}$–BPA complex.

The results above show that the direct and mediated detections of [Ru(bpy)$_3$]$^{2+}$ have been achieved. It is therefore interesting to

investigate whether the oxidized product of BPA in the presence of [Ru(bpy)$_3$]$^{2+}$ could be strongly adsorbed on the ITO surface and affect the activity of ITO electrode. As shown in Fig. 2b, repetitive DPVs of [Ru(bpy)$_3$]$^{2+}$–BPA complex in neutral medium indicates these anodic peaks I and III, which exhibit a significant decrease with increasing sweeping number. When the voltammetric sweeping reaches the 10th cycle, the two peaks (I and III) completely disappear. Combined with the SEM images in Fig. 3b, the oxidized products of BPA mediated by [Ru(bpy)$_3$]$^{2+}$ may be also adsorbed on the ITO electrode and hence hamper the electron transfer between ITO and BPA molecules. In addition, SEM in the presence of [Ru(bpy)$_3$]$^{2+}$ shows an image like seaweeds, revealing that [Ru(bpy)$_3$]$^{3+/2+}$ may be immobilized in the oxidized products of BPA in the process of repetitive DPVs. The proposition is supported by the CVs in Fig. 10. The dotted line shows a redox peak in buffer solution without [Ru(bpy)$_3$]$^{2+}$ at the formal potential of 1.004 V [52], corresponding to Ru(III)/Ru(II) reaction.

On the other hand, it is noteworthy that the redox reactions of peak II are not obviously blocked by the oxidized products of BPA, implying that the direct or mediated oxidation of BPA requires an adsorption process of reactant BPA on the electrode, therefore, the oxidation of BPA is hampered by the oxidized products of BPA. However, as depicted by Fig. 10, a pair of well-defined redox wave is observed on the ITO electrode modified by the electropolymerized films (curves 2 and 3), suggesting the oxidized products of BPA has the ability to mediate the electron transfer between polypyridyl ruthenium (II) complexes and ITO electrode. More interestingly, the
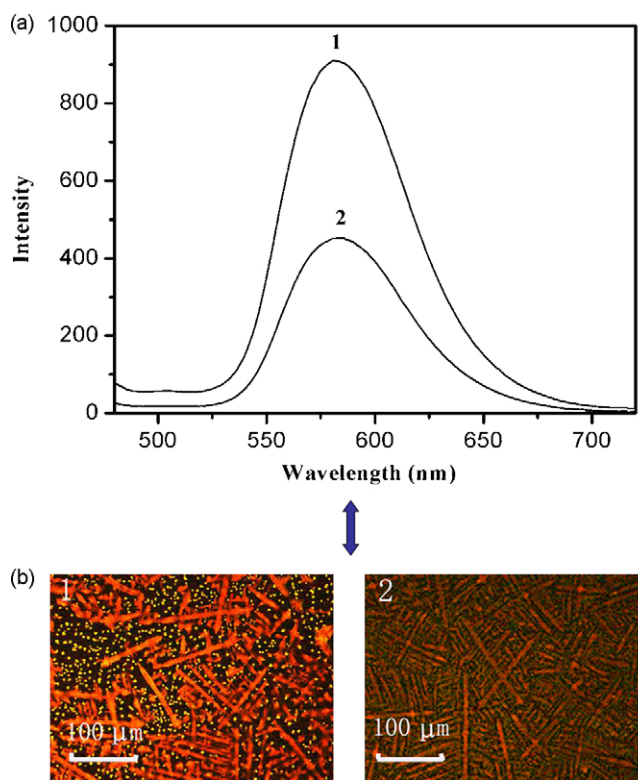
Fig. 6. Emission spectra (a) and fluorescence microscopic images (b) of $[Ru(bpy)_3]^{2+}$/ITO (1) and $[Ru(bpy)_3]^{2+}$–BPAox/ITO (2) electrode, respectively.
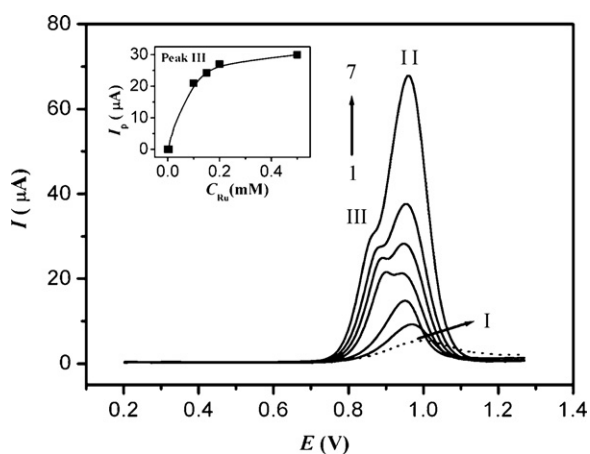
Fig. 7. DPVs of $0.06\,mmol\,L^{-1}$ BPA on the ITO electrode in solution of $0.2\,mol\,L^{-1}$ HCl with $[Ru(bpy)_3]^{2+}$ $(mmol\,L^{-1})$: (1) 0 (dotted line), (2) 0.005, (3) 0.01, (4) 0.10, (5) 0.15, (6) 0.20, (7) 0.50. The inset is a plot of the peak III current vs $[Ru(bpy)_3]^{2+}$ concentration.

electropolymerized films with $[Ru(bpy)_3]^{2+}$ may be not as compact as that in the absence of $[Ru(bpy)_3]^{2+}$, hence the former shows a more favorable electron transfer process. Of course, compared with the ITO surface (curve 4), the electropolymerized films indicate a weak inhibitor for the redox reaction of $[Ru(bpy)_3]^{2+}$.

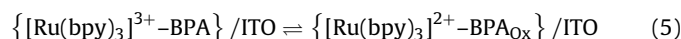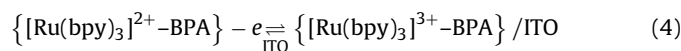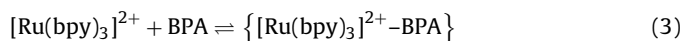Fig. 8. CVs of $0.2\,mmol\,L^{-1}$ $[Ru(bpy)_3]^{2+}$ on the ITO electrode in solution of $0.2\,mol\,L^{-1}$ HCl with BPA $(mmol\,L^{-1})$: (1) 0, (2) 0.005, (3) 0.01, (4) 0.02, (5) 0.04, (6) 0.06, (7) 0.08, (8) 0.10, (9) 0.12. Scan rate: (a) $0.05\,V\,s^{-1}$, (b) $0.80\,V\,s^{-1}$. The inset is plots of the peak III current (I_p) or peak II difference (ΔI) in the presence and absence of BPA vs BPA concentration.

Combined with all results mentioned above, the mediated oxidation of BPA by $[Ru(bpy)_3]^{2+}$ on the ITO electrode is proposed as follows:

$$[Ru(bpy)_3]^{2+} + BPA \rightleftharpoons \left\{[Ru(bpy)_3]^{2+} - BPA\right\} \tag{3}$$

$$\left\{[Ru(bpy)_3]^{2+} - BPA\right\} - e \underset{ITO}{\rightleftharpoons} \left\{[Ru(bpy)_3]^{3+} - BPA\right\} /ITO \tag{4}$$

$$\left\{[Ru(bpy)_3]^{3+} - BPA\right\} /ITO \rightleftharpoons \left\{[Ru(bpy)_3]^{2+} - BPA_{Ox}\right\} /ITO \tag{5}$$

3.3. Effects of interfering substances

To identify possible interferents which may affect the signal of peaks I and III, the effects of some metal ions, alcohol and phenol $(0.01\,mmol\,L^{-1})$ on the voltammetric response of BPA in the presence of $[Ru(bpy)_3]^{2+}$ have been examined. The results are summarized in Table 1, indicating a very small decrease in the response slope in the applied potential range. The voltammetric response displays a high selectivity for BPA with respect to Zn^{2+}, Cu^{2+}, ethanol and propanetriol. It is due to the oxidation of phenol mediated by $[Ru(bpy)_3]^{2+}$, phenol produces a larger increase in response slope. However, the direct oxidation of BPA on the

Table 1
Effects of various interferents $(0.01\,mmol\,L^{-1})$ on the voltammetric detection of BPA in the presence of $[Ru(bpy)_3]^{2+}$.

Interferents	None	Zn^{2+}	Cu^{2+}	Ethanol	Propanetriol	Phenol
Response slope ($\mu A\,\mu mol^{-1}\,L$)	0.220	0.215	0.218	0.213	0.211	0.256
Correlation coefficient	0.995	0.994	0.992	0.990	0.993	0.996
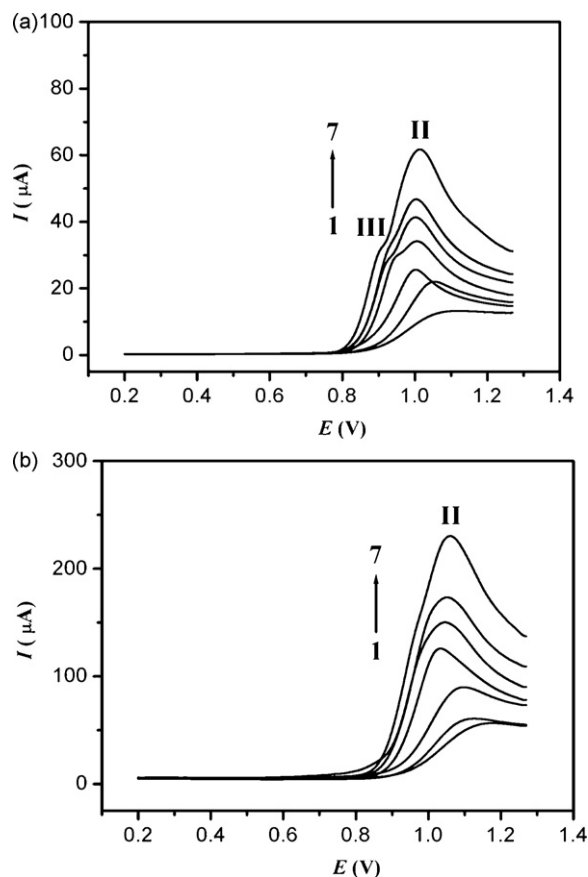
Fig. 9. Linear sweep voltammograms of 0.06 mmol L^{-1} BPA on the ITO electrode in solution of 0.2 mol L^{-1} HCl with [Ru(bpy)$_3$]$^{2+}$ (mmol L^{-1}): (1) 0, (2) 0.005, (3) 0.01, (4) 0.10, (5) 0.15, (6) 0.20, (7) 0.50. Scan rate (V s^{-1}): (a) 0.05, (b) 0.80.
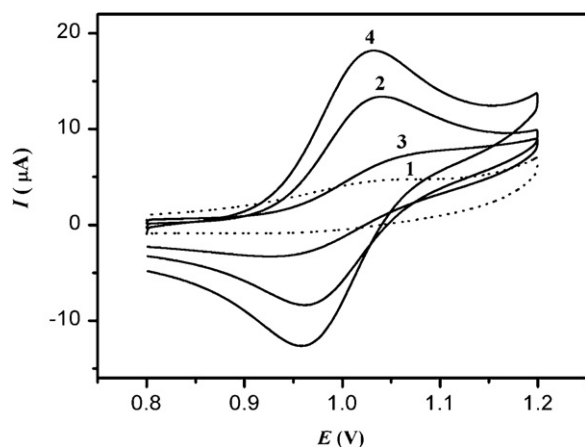
Fig. 10. CVs of [Ru(bpy)$_3$]$^{2+}$–BPAox/ITO electrode in pH 7.2 buffer solution in the absence (dotted line 1) and presence (solid line 2) of 0.1 mmol L^{-1} [Ru(bpy)$_3$]$^{2+}$. The solid lines 3 and 4 correspond to CVs of BPAox/ITO and ITO electrodes in buffer solution containing 0.1 mmol L^{-1} [Ru(bpy)$_3$]$^{2+}$, respectively.

ITO electrode is not basically disturbed by the presence of phenol.

4. Conclusions

Voltammetric technique by the mediation of polypyridyl ruthenium complexes has been developed for the detection of BPA. With this technique, the direct and mediated detections of BPA on the ITO electrode by [Ru(bpy)$_3$]$^{2+}$ is carried out. From this study, the following conclusions are derived.

(1) [Ru(bpy)$_3$]$^{2+}$ is an excellent mediator to induce the oxidation of BPA. The mediated detection of BPA is successfully achieved by monitoring the peak currents of [Ru(bpy)$_3$]$^{2+}$–BPA complex.
(2) For the mediated detection of BPA by [Ru(bpy)$_3$]$^{2+}$ on the ITO electrode at pH 7.2, the response current exhibits a linear range between 5 and 120 μmol L^{-1} with a sensitivity of 0.22 μA μmol^{-1} L. The detection limit is 0.29 μmol L^{-1} (S/N = 3) and the voltammetric response shows a high selectivity for BPA with respect to Zn^{2+}, Cu^{2+}, ethanol and propanetriol.
(3) By analyzing the effects of pH, scan rate and mediator concentration on the response of BPA oxidation, the oxidized mechanism of BPA mediated by [Ru(bpy)$_3$]$^{2+}$ on the ITO electrode is obtained.

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